Direct observation of adsorbed H_2-framework interactions in the Prussian Blue analogue $Mn^{II}_3[Co^{III}(CN)_6]_2$: The relative importance of accessible coordination sites and van der Waals interactions†

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Selective recovery of the guest–framework interactions for H_2 adsorbed in a nanoporous Prussian Blue analogue, through differential X-ray and neutron pair distribution function analysis at *ca.* 77 K, suggests that the H_2 molecule is disordered about a single position at the centre of the pore, (¼, ¼, ¼), without binding at accessible Mn^{II} sites.

Porous coordination framework materials capable of reversible H_2 sorption are of current interest for potential mobile energy-storage applications.[1–3] Pivotal to the rational development of host materials with increased H_2 storage capacities, approaching projected targets for practical applications, is the understanding of the nature of the H_2–framework interaction and the factors that influence H_2 binding strength and storage capacity. However, few structural studies have directly probed the adsorption sites in these systems when loaded with H_2.[4] As such, the principal mechanism for H_2 sorption remains controversial, with the current views developed from attempts to correlate observed sorption behaviour with the structural features and chemical functionality of the apo-host (*e.g.*, surface area and volume; surface polarisability and potential coordination sites). Of these, accessible coordination sites (or open metal sites) have been widely speculated to be involved in H_2 binding. Consequently, significant effort in the directed development of novel framework materials for H_2 storage is currently focused on the incorporation of accessible coordination sites.[2,5]

Recently, reversible H_2 uptake has been demonstrated in a family of nanoporous Prussian Blue analogues functionalised with perhaps the greatest (surface, volumetric and gravimetric) density of accessible coordination sites of any known coordination framework material (Fig. 1).[6,7] Here we directly probe the structure of local H_2–framework interactions within the H_2/D_2-loaded Prussian Blue analogue, $Mn^{II}_3[Co^{III}(CN)_6]_2$, using a differential pair distribution function (PDF) analysis of high-energy X-ray and neutron scattering data.[8] Contrary to current speculation, we find no evidence for binding interactions of the adsorbed H_2 with the accessible coordination sites. Instead, the H_2 molecule is disordered about a single site at the centre of the pore, (¼, ¼, ¼), which maximises van der Waals interaction with the pore surface lined with highly polarisable cyanide moieties.

The controversial nature of H_2 binding and the present lack of structural evidence for the proposed interactions are due, in part, to the inherent experimental challenge in "seeing" adsorbed H_2 molecules. The reversible (weak) nature of the H_2 binding within such porous materials typically results in dynamic disorder of the guest molecule that cannot be adequately resolved using conventional crystallographic analysis of Bragg scattering intensities, which probes only the *average* atomic positions. Furthermore, hydrogen has low X-ray scattering power relative to the framework atoms, often of similar magnitude to systematic errors in the data, and generally necessitates the use of neutron scattering.

The differential approach to PDF analysis applied here bypasses each of these difficulties. The PDF method recovers local atomic structure from diffraction data, in the form of a radial distribution function, without the assumption of translation symmetry imposed for Bragg analysis.[9] In the PDF, the intensity of correlations are weighted by the scattering power of *both* atoms involved, and, as such, the correlation between a strong scatterer and an otherwise weakly scattering atom can have a measurable contribution to the PDF. The differential PDF method directly probes molecular scale interactions associated with gas binding by selective recovery of only the atom–atom correlations (interatomic distances) arising from guest–framework or guest–guest interactions.[8] Here, the differential is obtained through direct subtraction of a reference PDF measured for the vacant framework from that of the guest-loaded framework, eliminating the contribution from host–host atomic correlations and reducing systematic errors.

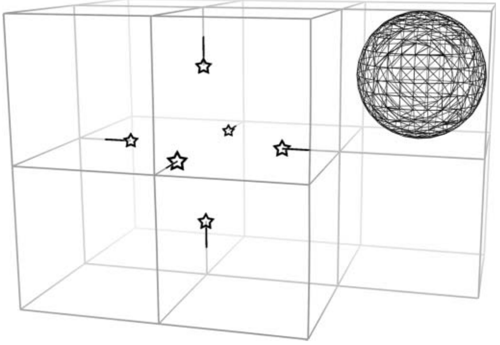

Fig. 1 Representation of the Prussian Blue network indicating the accessible Mn^{II} sites (star) surrounding a $Co(CN)_6^{3-}$ lattice vacancy. The lattice defines cavities of ∼4 Å diameter connected by larger cavities associated with the aperiodic $Co(CN)_6^{3-}$ vacancies at one-third of the Co^{III} sites.

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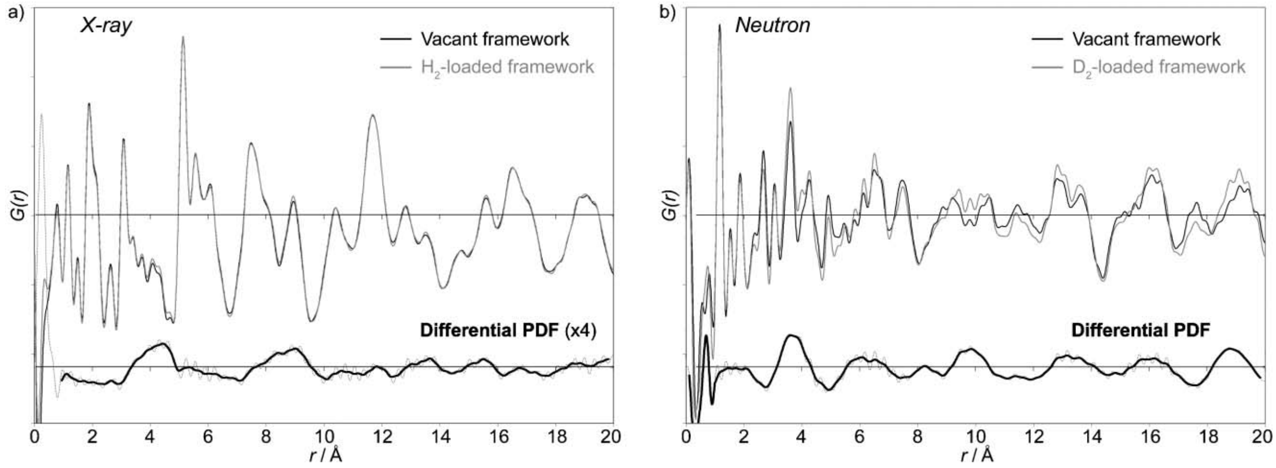

Fig. 2 The PDFs, *G(r)*, for the vacant and loaded framework and the corresponding differential PDFs from the X-ray (a) and neutron scattering data (b). The differentials, raw (dotted) and *r*-averaged over normalisation ripples (continuous), are shown.

The X-ray and neutron PDFs of the vacant and H_2/D_2-loaded framework were obtained from *in situ* diffraction data measured to moderately high values of momentum transfer ($Q_{\max} \sim 20.7$ Å^{-1} (Fig. 2). High-energy X-ray diffraction data (90.48 keV, λ = 0.1370 Å) were collected at the 11-ID-B beamline at the Advanced Photon Source, Argonne National Laboratory, using a General Electric amorphous silicon detector, for the desolvated framework at 80 K in nonadsorbing He and H_2 (99.999%) atmospheres under continuous gas flow and at 25 psi.[10–12] Neutron TOF diffraction data were collected at the general purpose powder diffractometer at the Intense Pulsed Neutron Source, Argonne National Laboratory, for the desolvated sample under vacuum and upon loading with D_2 gas (77 K, 1 atm) at 30 and 77 K.[13] For both X-ray and neutron experiments, H_2/D_2 loading conditions were as closely matched as possible to those under which sorption was measured (1.0 wt%, 1 atm, 77 K). This corresponds to an average of 0.5H_2 molecules per cubic cavity (*i.e.*, $Mn_3[Co(CN)_6]_2 \cdot 3.0\{H_2\}$).[6]

The X-ray differential PDF at 77 K contains only broad features dominated by H–metal and H–cyanide correlations. Further loading of the framework at 25 psi increased the intensity of the differential without changing its form. The neutron differential PDF at 77 K contains broad features dominated by D–cyanide correlations with an additional contribution from D–D correlations. The sharp peak at 0.700(2) Å corresponds to the D_2 single bond. The differential remained unchanged upon cooling to 30 K, except for a further sharpening of the D_2 single-bond peak.

Broad features in the differential PDFs are more consistent with a disordered guest than directional ordered binding to, for example, an accessible coordination site. Short-range binding interactions of the H_2/D_2 at accessible Mn^{II} sites should be evident as a relatively sharp peak in the differential PDF at 2–3 Å. No sharp features of this type are evident in either X-ray or neutron differential PDFs.

Differential PDFs calculated[14] for a model with a short-range binding interaction with Mn^{II}, fail to reproduce the features in the experimental data (Fig. 3). This is particularly evident in the X-ray differential, which contains a large contribution from the H–metal correlations. Calculated differentials based on a model consistent with van der Waals interactions, in which the guest H_2/D_2 is located at the centre of the pore, (¼, ¼, ¼), largely reproduces the observed peak positions and intensities of the X-ray and neutron differential PDFs. Slight deviations in the observed and calculated PDFs are most likely due to local ordering of the lattice vacancies on the 8–12 Å length scale, an effect not included in the simple structural model.

Thus, the qualitative features of the X-ray and neutron differential PDFs and quantitative modelling of the data suggest that at *ca.* 77 K the adsorbed H_2/D_2 molecules are disordered about the centre of the pores defined by the cubic framework, without interactions with the accessible Mn^{II} sites. Such interactions are not induced at lower temperatures, with no changes in the differential PDF at 30 K.

Rietveld refinement[15] of the neutron scattering data for the vacant framework at 30 K and 77 K was consistent with the

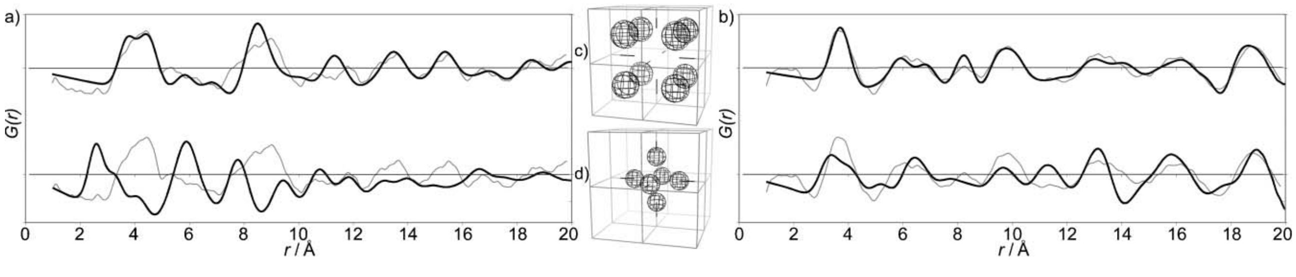

Fig. 3 Calculated X-ray (a) and neutron (b) differential PDFs for models consistent with van der Waals interactions (c, upper curves) and consistent with binding at the accessible Mn^{II} sites (d, lower curves). The experimental differentials (grey) are given for comparison.

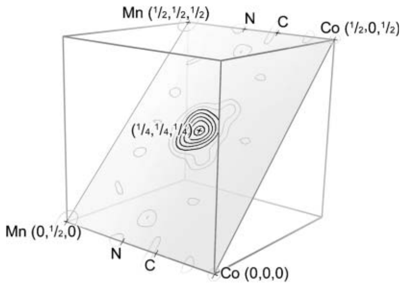

Fig. 4 Nuclear density Fourier difference map in the (011) plane from the Rietveld refinement of the D_2-loaded system at 77 K, modelling only framework atoms. Contours are drawn at 0.05 σ $Å^{-3}$ intervals. Levels below 0.15 (grey) are within the error in the data.

reported topology.[16] The slight expansion of the cubic lattice parameter upon D_2 sorption (0.028% and 0.036%) was significantly smaller than that evident upon N_2 sorption (0.36%), as is consistent with the larger kinetic diameter of N_2 ($\sim$3.6 Å).[8,17] Extensive changes in the peak intensities upon D_2 loading were associated with a broad residual nuclear density centred at (¼,¼,¼) when modelling only the framework atoms (Fig. 4). This residual was well modelled by a Gaussian distribution of nuclear density corresponding to a D_2 molecule with 50% occupancy, consistent with the established uptake,[6] further confirming the differential PDF analysis.

As established for other Prussian Blue analogues,[18] negative thermal expansion (NTE) of the $Mn_3[Co(CN)_6]_2$ framework was evident in both the vacant and D_2-loaded states between 30 and 77 K. The contraction of the lattice parameter upon heating by 0.036% and 0.027% correspond to estimated coefficients of thermal expansion of -7.6×10^{-6} K^{-1} and -5.8×10^{-6} K^{-1}, respectively. A reduced NTE effect in the guest-loaded framework is consistent with a steric dampening of the transverse cyanide vibrations underlying the NTE behavior.[18]

In light of the present structural study, we now propose that the different H_2 sorption enthalpies at *ca.* 77 K for the isostructural series of vacancy-containing Prussian Blue analogues, $M^{II}_3[Co^{III}(CN)_6]_2$ (M = Mn, Fe, Co, Ni, Cu, Zn),[7] are not principally due to the different affinity of H_2 for the accessible M^{II} sites, but instead correlate to the different complementarities of the pore cavity and curvature to the H_2 molecule ($\sim$2.8 Å kinetic diameter).[17,19] In this series, the pores ($\sim$4 Å diameter) are consistently larger than the H_2 molecule, capable of sorbing larger N_2 molecules, with higher sorption enthalpies in analogues with smaller pores/higher curvature. The pore/lattice dimensions, principally influenced by cation size[20] and crystal field considerations, follows the Irving–Williams series with an inverse trend seen for the sorption enthalpies.[7] We anticipate enhanced sorption behaviour in other Prussian Blue analogues with smaller pores tailored to fit the H_2 molecule, with the total uptake a combined function of the sorption enthalpy and sample microstructure (*i.e.*, crystallinity and particle size).

In summary, combined neutron and X-ray differential PDF analysis has provided the first conclusive structural elucidation of H_2 adsorbed within a molecular framework containing accessible coordination sites. We find no evidence for binding interactions with the accessible Mn^{II} sites, although this does not preclude the possibility of such interactions in other systems (perhaps those with hysteretic H_2 sorption behaviour or more with favourable orientation of the d-electrons). The differential PDF approach applied here can be readily extended to probe host–guest interactions in a broad range of materials with potential energy-storage applications, including other coordination framework materials, porous carbons and clathrates. Furthermore, we anticipate that the present results will redirect efforts in the targeted development of framework materials for H_2 storage towards pore geometries that best complement the H_2 molecule to maximise interactions with the pore surface.

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